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September 3, 2015

National Freedom of Information Officer
U.S. EPA
1200 Pennsylvania Avenue, NW (2822T)
Washington, DC 20460

Re: FOIA Request

To Whom it May Concern:

Pursuant to the Freedom of Information Act, 5 U.S.C. § 552, I hereby request copies of the following documents:

- All documents prepared or received for and all data and information collected and analyses related to East Liverpool, Ohio done in connection with the accepted manuscript in the Journal of the Air & Waste Management Association, entitled *Characterization of Air Manganese Exposure Estimates for Residents in Two Ohio Towns*, attached as Exhibit A, (the "Manganese Journal Paper"), including but not limited to, air modeling, ambient air monitoring, fingerprinting analyses, and information on exposure assessments.

- All fingerprint results, analyses, and reports related to manganese from particulate matter samples collected from Marietta, Ohio and East Liverpool, Ohio done by the U.S. EPA National Enforcement Investigations Center (NEIC), including, but not limited to the reports, results and analyses from using LA-ICP-MS (laser ablation-inductively coupled plasma- mass spectrometry), SEP (scanning electron microscopy), and XRD (X-ray diffractometry) techniques on such samples.

- All communications (both electronic and hard copy), including attachments and enclosures, between Dr. Danelle Lobdell (USEPA Triangle Park) or Edward Hudgens (USEPA Triangle Park) and any of the following persons in connection with the Manganese Journal Paper: Dr. Michelle A. Colledge (ATSDR Region 5); Jamie R. Julian (USEPA Region 5); Dr. Rosemarie M. Bowler (San Francisco State Univ.); Vihra V. Gocheva (San Francisco State University); Dr. Cheryl L. Beseler (Colorado State University); Dr. Harry A. Roels (Louvain Centre for Toxicology and Applied Pharmacology); Dr. George Bollweg (USEPA Region 5); Jamie Wagner (USEPA Region

5); ; Dr. Erin Haynes; Barbara Driscoll (USEPA); Dr. Mark Johnson (ATSDR); and/or Rebecca Geyer (USEPA Region 5).

We will pay all reasonable search and copying costs, up to $250. Should the cost of fulfilling this request exceed $250, please contact me. Alternatively or in addition to providing the requested documents, we would be happy to visit in-person for a file review of the requested records. If you have any questions regarding this request, please contact me. Thank you for your attention to this matter.

Regards,

/s/ Jessica L. Sharrow

EXHIBIT A

Journal of the Air & Waste Management Association
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/uawm20

Characterization of Air Manganese Exposure Estimates for Residents in Two Ohio Towns

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Characterization of Air Manganese Exposure Estimates for Residents in Two Ohio Towns

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Abstract

This study was conducted to derive receptor-specific outdoor exposure concentrations of Total Suspended Particulate (TSP) and respirable (dae≤10 μm) air manganese (air-Mn) for East Liverpool and Marietta (OH) in the absence of facility emissions data, but where long-term air measurements were available. Our "site-surface area emissions method" used U.S. EPA's AERMOD dispersion model and air measurement data to estimate concentrations for residential receptor sites in the two communities. Modeled concentrations were used to create ratios between receptor points and calibrated using measured data from local air monitoring stations.

Estimated outdoor air-Mn concentrations were derived for individual study subjects in both towns. The mean estimated long-term air-Mn exposure levels for total suspended particulate were 0.35 μg/m3 (GM) and 0.88 μg/m3 (AM) in East Liverpool (range: 0.014-6.32 μg/m3) and 0.17 μg/m3 (GM) and 0.21 μg/m3 (AM) in Marietta (range: 0.03-1.61 μg/m3). Modeled results compared well to averaged ambient air measurements from local air monitoring stations. Exposure to respirable Mn particulate matter (PM10) was higher in Marietta residents.

Implications

Few available studies evaluate long-term health outcomes from inhalational manganese (Mn) exposure in residential populations, due in part to challenges in measuring individual exposures.

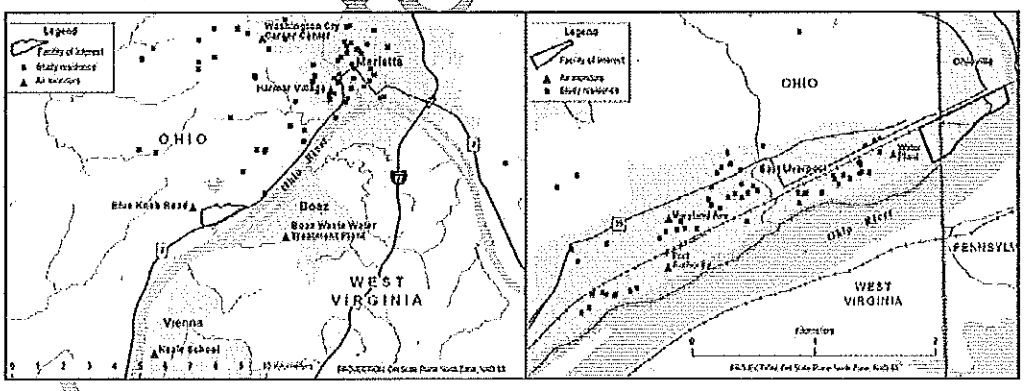
Local long-term air measurements provide the means to calibrate models used in estimating long-term exposures. Furthermore, this combination of modeling and ambient air sampling can be used to derive receptor-specific exposure estimates even in the absence of source emission data for use in human health outcome studies.

Introduction

Only a few inhalation exposure studies have evaluated non-occupational, stationary source-based environmental exposures to manganese (Mn). Although Mn inhalation exposure in the general population is much lower than in the occupational setting, these studies also identified subtle neurological deficits in residential populations chronically exposed to low air-Mn levels

(Baldwin et al. 1999; Beuter et al. 1999; Bowler et al. 1999; Lucchini et al. 2012; Menezes-Filho et al. 2011; Mergler et al. 1999; Riojas-Rodriguez et al. 2010; Rodriguez-Agudelo et al. 2006).

The first account of Parkinsonian symptoms linked to inhalation exposure of Mn was documented by Couper (1837). Since then, the epidemiologic literature has established that adverse neurological and neuropsychological health effects are associated with chronic exposure to excessive airborne manganese (air-Mn) via inhalation. Occupational studies have described motor impairment (e.g., psychomotor speed, reaction time, hand-eye coordination, postural sway), cognitive deficits (e.g., verbal IQ, working memory), mood perturbations (e.g., depression, anxiety), and depressed olfaction in workers (microsmia, anosmia) with average Mn exposures as low as 32 $\mu g/m^3$, with increasing severity for higher exposures [Agency for Toxic Substances and Disease Registry (ATSDR) 2012; Blond and Netterström 2007; Bowler et al. 2006, 2007, 2011; Chia et al. 1995; Iregren 1990; Lucchini et al. 1995, 1999; Mergler et al. 1994; Roels et al. 1985, 1987, 1992, 1999, 2012].



Environmental air-Mn concentrations in the United States vary significantly with location and proximity to emissions sources. Based on national air monitoring networks, the average

background air-Mn concentration in urban areas is approximately 0.05 $\mu g/m^3$ [United States Environmental Protection Agency (U.S. EPA) 2012a]. U.S.EPA (1984) reported that rural air-Mn from 1965-1982 was approximately 6.25 times lower than urban air-Mn. Air-Mn in areas with Fe/Si-Mn (iron/silicomanganese) alloy smelters or other operations using Mn-containing products can be several orders of magnitude higher than what has been reported in rural and urban environments (ATSDR 2007, 2009, 2010, 2012; U.S. EPA 1984, 2012a).

Two communities in Eastern Ohio were identified with elevated measured concentrations of ambient air-Mn, one of which has the highest concentrations of measured air-Mn reported to the U.S.EPA Air Quality System (AQS) database (U.S.EPA 2012a). Air-Mn in one community (Marietta) is predominantly released from a large Fe/Si-Mn alloy smelting plant (Eramet, Inc.) while in the other community (East Liverpool), it is released during the offloading, grinding (for resizing), packaging, and storage of Mn-containing ore and alloy products at a metals storage and packaging facility (S.H. Bell Company). East Liverpool is approximately 200 km north-northeast of Marietta, along the Ohio River.

Residents from each community were recruited to participate in a study examining neurological and neuropsychological impacts from chronic exposures to low levels of outdoor air-Mn. In support of this epidemiologic study, modeled estimates of outdoor air-Mn concentrations were derived as surrogates of outdoor exposure for residents identified as study participants in the two communities. Dispersion modeling calibrated with measured data was used to estimate ambient air-Mn exposures for each study participant in the two towns. Both communities had over 10 years of environmental total suspended particulate (TSP) sampling data generated between 1999

and 2013 that were analyzed for a number of toxic metals, including Mn. Only years where data met 75% completeness in both towns (2003-2013) were used for statistical analyses.

The objective of this study was to estimate inhalation exposures by deriving residence-specific outdoor air-Mn for two Ohio communities.

Materials and methods

Stationary monitoring and fingerprinting of ambient TSP air-Mn

24-hour TSP samples have been continuously collected and analyzed by the Ohio Environmental Protection Agency, Division of Air Pollution Control (Ohio EPA) in both communities since 2003 (Ohio EPA 2012a,b), though 10 months of continuous data were also collected in 2000 in East Liverpool. Stationary high volume ("HiVol") monitors used in these communities pull ambient air through an orifice at the top of the monitor at a volume rate of 1.13 m^3/min and particulate matter is deposited on a 203 x 254-mm glass fiber filter according to U.S.EPA Compendium Method IO 2.1 (U.S. EPA 1999a). The concentration of TSP was reported as mass of particulate matter collected per cubic meter of air sampled ($\mu g/m^3$) at sea level pressure (1 atm) and a temperature of 25°C (ATSDR 2007). Sample filters were analyzed for metals using inductively coupled plasma/mass spectrometry (ICP/MS) according to the U.S.EPA Compendium Method IO 3.5 (U.S. EPA 1999b).

At both sites, 24-hour TSP filter samples are collected in community air monitoring stations every 6 days. These 24-hour samples are composited and analyzed to yield a monthly average

air-Mn concentration (Ohio EPA 2012a,b). Because composite sample concentrations of Mn were elevated, in 2005, Ohio EPA began analyzing every filter from the East Liverpool Water Plant air monitoring station in individual 24-hour samples (discrete) as well as monthly composite samples to yield more information about the magnitude of Mn levels in community outdoor air (Ohio EPA 2012b). Thus, data at this location were evaluated as both 24-hour and monthly averaged composite samples (ATSDR 2010).

To understand the sources and toxicological implications of outdoor exposure to air-Mn, the U.S. EPA National Enforcement Investigations Center (NEIC) Laboratory analyzed Mn in particulate matter collected on 341 glass fiber HiVol 24-hour sample filters at stationary sampling locations in Marietta and East Liverpool for fingerprint analysis. These analyses were carried out to yield information about how metals on the filters at various locations are related and compare to source samples, evaluate size distribution and morphology of collected particles, and determine the elemental abundance and chemical form of metals on the filters. For the purposes of these analyses, air filters were evaluated by using LA-ICP-MS (laser ablation- inductively coupled plasma- mass spectrometry), SEM (scanning electron microscopy), and XRD (X-ray diffractometry) techniques (U.S. EPA 2010a,b).

Size fractions of particulate matter in East Liverpool air samples were also determined from collocated air monitors at the Water Plant operated by Ohio EPA and U.S. EPA. The monitors collected 24-hour TSP, PM_{10}, and $PM_{2.5}$ samples for three months in summer of 2011. These samples were collected during the period that health outcome data were collected in the community, and is the only sampling period that analyzed data in all three particle fractions.

To estimate exposures to respirable manganese, the TSP air-Mn concentration was multiplied by the fraction of air-Mn PM_{10}, and $PM_{2.5}$ as determined by fingerprinting analysis in Marietta (PM_{10} (0.83 or 83%) and $PM_{2.5}$ (0.21 or 21%), and by collocated monitoring data in East Liverpool (PM_{10} (0.35 or 35% and $PM_{2.5}$ (0.037 or 3.7%).

Identification of Modeling Receptor Points

Receptor points consisted of monitoring stations and the residential location of people recruited as part of two population studies that examined the potential health effects of outdoor air-Mn exposure in adult residents of Marietta, Ohio (n=100) and East Liverpool, Ohio (n=86). Study participants for each community were identified based on the likelihood of elevated exposures. The study participants were obtained by random recruitment in these areas and application of eligibility criteria as described for Marietta elsewhere (Bowler et al. 2012; Kim et al. 2011). Study subjects had neuropsychological tests and provided blood and serum samples for analysis. Data collection in these communities took place in 2009 and 2011 for Marietta and East Liverpool, respectively.

Model methodology

AERMOD is U.S. EPA's preferred dispersion model for short-range (less than 50 km) modeling analyses. The AERMOD modeling system consists of two preprocessors and a dispersion model (Cimorelli et al. 2005):

- A meteorological preprocessor (AERMET) uses meteorological data and surface characteristics to develop planetary boundary layer parameters to create profiles of wind, turbulence, and temperature;

- A terrain preprocessor (AERMAP) uses gridded terrain data to determine the influence of elevation on the modeling domain, which allows AERMOD to calculate concentrations in either flat or complex terrain;

- A steady-state plume model (AERMOD) designed to estimate impacts in urban or rural areas, in flat or complex terrain, for surface or elevated releases from multiple sources and multiple source types.

Land use/land cover data and one arc-second (approximately 30 m) National Elevation Dataset for the study areas were acquired from the United States Geological Survey Seamless Server (USGS). Weather data were acquired from the nearest National Weather Service (NWS) stations for the two communities which provided current hourly surface observations and upper air sounding data (National Climatic Data Center, NCDC).

AERMOD was used to predict long-term (5-year) average air-Mn concentrations at each modeled receptor. The model inputs for the two towns are as follows:

- Marietta: the nearest NWS surface station is located at the Mid-Ohio Valley Regional Airport in Parkersburg, WV, approximately 8 km east-southeast of the facility. The nearest NWS upper air station with data for the same 5-year period is at the Wright-Patterson Air Force Base in Dayton, OH, which is approximately 322 km west-northwest of the facility. Five

consecutive years of surface and upper air meteorological data (1991-1995) were processed through AERMET (U.S.EPA 2010c) for the Marietta modeling.

- East Liverpool: the nearest and most representative meteorological station is located at the Pittsburgh International Airport in Pittsburgh, PA, which is approximately 40 km southeast of the facility. NCDC 1-minute surface data, NWS hourly surface data, and NWS upper air data are all available for this station. Five consecutive years of data (2006-2010) were processed through AERMET (U.S. EPA 2012b) for the East Liverpool modeling.

Calculating exposure estimates

No emissions data were available for the metals packaging and storage facility in East Liverpool, thus an approach was used for estimating residential exposures that is scalable to measured data for both towns (herein referred to as "*site-surface area emissions method*"). To estimate outdoor residential air-Mn concentrations for each study subject residence, AERMOD was used to determine air-Mn concentration ratios of each residence to a reference air monitoring station (RAMS). In Marietta, the long-running Washington County Career Center (WCCC) monitor was used as the reference point, and in East Liverpool, the Maryland Avenue monitor was chosen to be the reference point. Reference point selection was based on how well measured data at each site predicted measurements at the other sites using the scaling and modeling method detailed below.

Unlike traditional dispersion modeling where detailed emissions data are available, the approach we are proposing assumes the entire surface area of the site is a single area emissions source.

AERMOD was used to calculate 5-year average air concentrations from a scalable unit emission rate of 1 gram per second (g/s) over the full extent of the property of each facility. Dispersion modeling is linear, thus choosing a scalable unit emission rate facilitates calculating estimated outdoor concentrations from many on-site sources without re-running the model for each source. This procedure is recommended for dispersion modeling (U.S. EPA 2005).

The unit emission rate was used for modeling purposes to calculate ratio relationships between estimated air-Mn concentrations at receptor points. Using this approach, the relationships of the modeled concentrations to each other and to a known reference point (in the form of estimated outdoor exposure ratios) can be used to calculate outdoor air-Mn concentrations at the residence of each study participant. In this instance, the known reference point was historical data recorded at the WCCC and Maryland Avenue outdoor air monitoring stations. AERMOD outputs for estimated outdoor air-Mn were scaled to actual measurements at the monitoring stations, yielding a relative fraction of air-Mn measured at the monitoring stations for all receptor points. For calculating residential outdoor exposure estimates annual average air-Mn measurements were used to derive outdoor exposure concentrations from air-Mn ratios calculated using AERMOD modeling outputs. The method for calculating the estimated outdoor exposure of each receptor point was defined as:

$$R(\text{air}-\text{Mn}) = \frac{\text{AR}\left(\frac{\mu g}{m^3}\right)}{\text{RAMS}\left(\frac{\mu g}{m^3}\right)} \text{x } C(\mu g/m^3) \qquad 1$$

where R(air-Mn) is the outdoor exposure concentration of air-Mn for each receptor; AR is the receptor-specific AERMOD estimate of air-Mn derived from the unit emission rate of 1 g/sec; RAMS is the AERMOD estimate of air-Mn derived from the unit emission rate at the reference air monitoring station; and C is the annual average air-Mn concentration measured at the reference air monitoring station.

Statistics

Raw data from area air monitors were obtained in Microsoft Excel files. Descriptive statistics, including confidence intervals, standard deviation, means, and quartiles were generated to compare measured and modeled data for each town. Annual and rolling 5-year averages of ambient Mn concentrations were calculated for air monitoring sites where sufficient data were available to make a comparison to modeling estimates. Scaling factors were derived from measured levels of Mn in the PM_{10} and $PM_{2.5}$ fractions of air-Mn TSP and were used to estimate residential exposures to respirable air-Mn. Descriptive statistics were generated to qualitatively compare measured and modeled data for each town, and exposure ratios and estimates were calculated using Microsoft Excel 2007.

Results

Stationary sampling data of TSP air-Mn

The statistical summary for the five Marietta air monitor locations (Table 1) shows that over the 10-year sampling period (2003-2013), TSP air-Mn samples frequently exceeded the background

values typical of ambient air-Mn in urban areas (U.S. EPA 2012a). Across the five sampling sites, the arithmetic mean (AM) of the monthly composite air-Mn concentrations ranged from 0.11 $\mu g/m^3$ to 0.39 $\mu g/m^3$. For comparison, the Mn concentrations for eight 24-hour samples collected on the facility property ranged from 0.46 to 1.90 $\mu g/m^3$ and averaged 1.13 $\mu g/m^3$ (AM) and 1.04 $\mu g/m^3$ (GM, geometric mean). In East Liverpool, the majority of monthly air-Mn concentrations also exceeded the national background average. Across the three sampling sites the monthly AM ranged from 0.17 to 1.42 $\mu g/m^3$ (Table 2). Air-Mn concentrations for 24-hour samples (Water Plant) ranged from 0.02 to 25.0 $\mu g/m^3$ and averaged 1.50 (AM) and 0.56 $\mu g/m^3$ (GM) (Table 2). TSP air-Mn in both communities exceeded the U.S.EPA reference concentration (RfC=0.05 $\mu g/m^3$; U.S.EPA 2012c) and/or the ATSDR minimal risk level (MRL=0.30 $\mu g/m^3$; ATSDR, 2012) for at least one community monitoring site in nearly every reported measurement date during the 10 year sampling period.

The SEM analyses used by NEIC for particle fingerprinting indicated that in Marietta 77% of the ambient air-Mn particulate matter on the filters was predominately spherical and that the chemical form of Mn was generally Mn-oxide. The analysis also determined that 83% of TSP air-Mn met the World Health Organization (WHO 1999) definition of respirable with Mn particles having an aerodynamic diameter (d_{ae}) $\leq$ 10 μm (PM_{10}) and 21% with a $d_{ae} \leq 2.5$ μm ($PM_{2.5}$). More than half of the Mn particles had a d_{ae} ranging from 3.4 to 4.6 μm. The high prevalence of fine Mn particles in Marietta is consistent with the fine metal dusts released from high-heat processes, such as smelting (U.S. EPA 1996).

In 2011, collocated air monitors were sited and operated by Ohio EPA and U.S.EPA at the East Liverpool Water Plant location for collection of 24-hour TSP, PM_{10}, and $PM_{2.5}$ samples. From these samples, it was determined that TSP from East Liverpool has a greater percentage of non-respirable Mn particles compared to Marietta TSP. In East Liverpool, 35% of TSP air-Mn consisted of PM_{10} Mn whereas only 3.7% of the TSP air-Mn was $PM_{2.5}$ Mn. This is consistent with SEM fingerprinting analysis conducted by NEIC on a limited number of East Liverpool TSP filters indicating that Mn particles in East Liverpool have a d_{ae} range of 4.4 to 24.3 µm (U.S. EPA 2010b). Compared to Marietta, a generally larger Mn particle fraction was expected given that emission points at the source facility in East Liverpool are general offloading, storage, and sizing/grinding operations. Estimated annual concentrations of PM_{10} Mn and $PM_{2.5}$ Mn were generated using the ratios determined from fingerprinting and monitoring, and descriptive statistics were generated to compare residential outdoor exposure concentrations in the communities.

Residential Outdoor Exposure Concentrations

Given that the East Liverpool plant did not have facility-specific Mn emissions data, the *site-surface area emissions method* was used for both towns to yield comparable estimates of exposure. Table 3 shows a comparison of average (AM) measured community sampling data for all monitoring sites (2003-2013) and modeled long-term outdoor exposure concentrations of TSP air-Mn in Marietta and East Liverpool. In Marietta, the modeled outdoor exposure concentrations ranged from 0.03 µg/m^3 at the lowest receptor point to 1.61 µg/m^3 at the highest receptor point, with an average outdoor exposure concentration for all receptor points (n=100) of 0.21 µg/m^3

(AM) and 0.17 $\mu g/m^3$ (GM). Across the sampling period in East Liverpool, the modeled outdoor exposure concentrations of TSP air-Mn ranged from 0.014 $\mu g/m^3$ at the lowest exposed receptor point to 6.32 $\mu g/m^3$ at the highest exposed receptor point, with an overall average outdoor exposure concentration for all receptor points (n=86) of 0.88 $\mu g/m^3$ (AM) and 0.35 $\mu g/m^3$ (GM). The statistical distribution of modeled TSP air-Mn were within the range of measured air-Mn outdoor exposure concentrations across all monitors located in each community (Table 3), which provides internal consistency for the calculation approach used in the present study.

Descriptive statistics were calculated for the fraction of modeled TSP air-Mn estimated to be PM_{10} and $PM_{2.5}$ using scaling factors derived from the fingerprinting analyses for the Marietta study and collocated measurements for the East Liverpool study. Table 4 presents the statistical distribution of these estimates in Marietta [PM_{10}: 0.18 $\mu g/m^3$ (AM), range 0.03 to 1.33 $\mu g/m^3$; $PM_{2.5}$: 0.05 $\mu g/m^3$ (AM), range 0.007 to 0.34 $\mu g/m^3$] and East Liverpool [PM_{10}: 0.31 $\mu g/m^3$ (AM), range 0.005 to 2.21 $\mu g/m^3$; $PM_{2.5}$: 0.03 $\mu g/m^3$ (AM), range 0.001 to 0.23 $\mu g/m^3$]. Results indicate that even though the TSP air-Mn levels in East Liverpool were generally higher than in Marietta, the Marietta residents have a higher exposure to respirable Mn particulate matter.

Method Validation

Traditional dispersion modeling based on highly detailed facility-reported Mn emission estimates was performed to estimate study participant exposures in Marietta, which was detailed elsewhere (U.S. EPA 2010c; Bowler et al. 2012). In summary, 255 tons per year of manganese was modeled as released via 15 point sources and 193 volume sources modeled from three overarching processes at the Eramet facility: 1) furnace emissions (melting, tapping, charging,

hot metal transfer, feed system, slag handling, and casting); 2) the metal oxygen reduction process (including the pelletizer); and 3) materials handling processes (including conveying, loading/unloading, feed systems, hoppers, crushing, sizing, packing, milling, and bagging). These detailed emissions data were provided under a regulatory request for information to the U.S. EPA. This type of information is not readily available for general research outside of environmental enforcement agencies. In that evaluation, two long-term air-Mn monitoring stations in Marietta were useful for comparing modeled 5-year averages with measured 5-year averages: the WCCC monitoring station, which has been in operation since 2000, and the Harmar Village monitoring station, which has been in operation since 2007. The rolling 5-year measured average for eight periods at the WCCC (0.16 $\mu g/m^3$) compared well to traditional dispersion modeling 5-year ambient outdoor air-Mn estimates at the WCCC air monitoring site (0.14 $\mu g/m^3$), suggesting that for Marietta the traditional dispersion model accurately predicts long-term ambient Mn concentrations at the WCCC monitoring site (Table 5). Harmar Village has two 5-year periods from which to calculate a rolling 5-year average. Comparison to the Harmar Village data is not ideal, since production at the Eramet plant has diminished in recent years, negatively biasing long-term averaging for prior years. Even still, the predicted dispersion modeling concentration at this location (0.16 $\mu g/m^3$) and the measured average (0.11 $\mu g/m^3$) of the 2007-2011 and 2008-2012 periods were within an order of magnitude (Table 5) and would likely have been closer if measured data from years with greater air-Mn emissions had been available.

In Marietta, WCCC and Harmar Village had the greatest number of observations (n>50) over the period 2003-2013. WCCC is the reference location and by default the *site-surface area emissions*

method estimates are perfectly correlated with the long-term air measurements at this site. Only Harmar Village in Marietta could be used to compare dispersion modeling based on emissions data to the *site-surface area emissions method* model estimates of air-Mn. In general, the modeled average of air-Mn as generated by the traditional dispersion model (0.16 $\mu g/m^3$) was slightly more accurate than the *site-surface area emissions method* model estimate (0.18 $\mu g/m^3$) at this location. Both modeling runs overestimated the actual measured concentration at the site, which was 0.11 $\mu g/m^3$ over the 2003-2013 sampling period. The number of observations for air-Mn measurements at the three other Marietta monitoring locations was too low at Blue Knob Road (n=25), Boaz Waste Water Treatment Plant (n=12), and Neal Elementary (n=12) to yield a meaningful comparison between the facility-specific emissions model and *site-surface area emissions method.* The comparison of the traditional dispersion model to air measurements (model-to-air measurements) and the facility-specific emissions model to the *site-surface area emissions method* (model-to-method) at the Harmar Village monitoring site indicates that *the site-surface area emissions method* yields reasonable exposure estimates.

Discussion

Public health concern regarding air-Mn exposures has been acknowledged since the 1970s and probably earlier (Joselow et al. 1978). Government regulation for anthropogenic sources stemming from these health concerns and epidemiologic research on long-term low-level inhalation exposure to Mn in ambient air began in the United States with the publication of a U.S.EPA reference concentration (RfC) value of 0.050 $\mu g/m^3$ in 1993 (U.S. EPA 2012c). RfC supporting documents initially focused on the potential risk of Mn emissions from mobile

sources from the combustion of the gasoline additive methyl-cyclopentadienyl manganese tricarbonyl (MMT) (Davis et al. 1998). However, subsequent studies have suggested that industrial sources of air-Mn may have greater impacts to ambient air than motor vehicle exhaust from the combustion of gasoline containing MMT (ATSDR 2012).

Existing studies have generally lacked personal air monitoring and completely rely on area monitoring to yield an understanding of study subject exposures. Those that did have personal air monitoring to estimate study subject exposures only had a few days of air sampling in the study. The *site-surface area emissions method* is proposed as a tool that yields long term estimates of individual study subject exposures to address this research data gap.

Comparison to TSP air-Mn studies

The mean air-Mn concentrations measured in Marietta and East Liverpool are comparable to those reported in other studies documenting adverse health effects in Mn-exposed communities. The ranges of monthly composite TSP air-Mn averages across all sites sampled between 2003 and 2013 were 0.11 $\mu g/m^3$ to 0.39 $\mu g/m^3$ in Marietta and 0.17 to 1.50 $\mu g/m^3$ in East Liverpool. A community study in Quebec that identified neuromotor and neuropsychological deficits and mood changes reported an average TSP air-Mn concentration of 0.022 $\mu g/m^3$ with a range of 0.009-0.035 $\mu g/m^3$ (Baldwin et al. 1999; Beuter et al. 1999; Bowler et al. 1999; Mergler et al. 1999). In this study, four days of ambient air sampling were available to assess inhalation exposures, but personal exposure estimates were not available.

Comparison to PM_{10} air-Mn studies

Estimated PM_{10} air-Mn exposures derived from measured and modeled data yielded a long-term average (AM) air-Mn concentration of 0.18 $\mu g/m^3$ for Marietta and a long-term average (AM) air-Mn concentration of 0.31 $\mu g/m^3$ for East Liverpool. Rodriguez-Agudelo et al. (2006) reported a statistically significant association between air-Mn concentrations and altered neuromotor function in Mexicans living at various distances from Mn mining operations where limited samples collected at 28 residences in 8 communities had a mean PM_{10} air-Mn concentration of 0.42 $\mu g/m^3$. Personal exposure estimates were not available to conduct regression analyses of motor test results; however, residents living nearest air monitors with elevated exposures were identified as having a higher risk of motor dysfunction. Lucchini et al. (2012) reported deficits in olfactory and motor function in Italian adolescents exposed to elevated levels of PM_{10} air-Mn from historical ferro/Mn alloy operations with an average PM_{10} air-Mn concentration of 0.05 $\mu g/m^3$ post-facility closure and average soil Mn of 958 mg/kg. While the latter study did not note associations between air-Mn levels and health outcomes, adverse health outcomes had statistically significant associations with soil Mn levels. This Italian study highlights the significance of deposition, particle transport, and distance from source in the understanding of cumulative exposures. However, multiple confounders complicate the interpretation of these results, including a limited personal air sampling duration of 24 hours.

Comparison to $PM_{2.5}$ air-Mn studies

In Brazil, a reduction in cognitive function was noted in mothers and their children who were exposed to ferro/Mn alloy emissions where $PM_{2.5}$ air-Mn averaged 0.15 $\mu g/m^3$ (Menezes-Filho et al. 2009, 2011), but only seven 24-hour samples were collected in a single location for this study. In the present study, estimated $PM_{2.5}$ air-Mn based on modeled and measured data averaged 0.05 and 0.03 $\mu g/m^3$ in Marietta and East Liverpool, respectively. Haynes et al. (2012) conducted a study in Marietta to evaluate the $PM_{2.5}$ air-Mn exposure levels in 38 children by collecting limited personal (two consecutive days in 2009 and 2010) and stationary (three 48-hr samples/week during two months in 2009 and 4 months in 2010) $PM_{2.5}$ air samples. The GM concentrations of $PM_{2.5}$ air-Mn collected during the study were reported to be 0.008 $\mu g/m^3$ for the personal samples and 0.011 $\mu g/m^3$ for the stationary samples.

Limitations

A number of non-quantified parameters exist that may influence the extent to which outdoor air-Mn relates to exposures. Only outdoor residential concentration estimates could be derived from available data, which excludes other important contributions to overall exposures, such as outdoor-indoor transport of particles. The results of this analysis do not include parameters such as activity patterns, deposition, and residential and resuspended Mn from ambient sources; however, ratios derived from modeled long-term average air-Mn concentrations can be used for a surrogate of inhalation exposure.

Emission rates are not likely to be consistent from year to year, so the assumption that any unit emission rate is constant and represents long-term emissions could result in over or under-predicting ambient concentrations for individual years. However, the comparison of modeled and measured data (Table 3) suggests that the model creates reasonable estimates of long-term ambient concentrations. The *site-surface area emissions method* is limited by its lack of facility-specific emissions data but uses the same terrain and meteorological preprocessors as site-specific emissions modeling. However, comparison of the two modeling analyses performed for Marietta shows that most estimates are only slightly higher for the *site-surface area emissions method* compared to facility-specific emissions modeling. A similar comparison was not possible in East Liverpool given the lack of Mn emissions data from on-site sources. However, the ratio approach allows for the easy adjustment of ambient Mn concentrations to reflect measured ambient ranges of air-Mn. If topographic data and site-specific meteorological data are available, receptor concentration ratios should be sufficiently precise to allow calibration with measured data from a reference air monitoring station as was noted in Marietta.

Potential uncertainties with the meteorological data used in Marietta may exist as well. The hourly surface data used in the Marietta modeling is from 1991-1995, which was chosen at the time due to concerns about the collection and reporting of newer data. While these concerns have now been addressed by the availability of 1-minute surface data, these data were not readily available at the time of the Marietta modeling. The upper air data used in Marietta was from a station 322 km away; however upper air data are regionally representative (as opposed to locally representative surface data). Additionally, complex terrain in the vicinity of both Marietta and East Liverpool can affect the predicted concentrations. While terrain elevations were taken into

account in the modeling, higher data resolution could affect estimated concentrations. Mn emissions calculations are impractical at the East Liverpool facility because of the highly variable loading, grinding, and packaging schedule, along with constantly changing production activities. Due to the lack of facility-specific emissions information in East Liverpool, the source parameters and emission rates for the facilities were based entirely on generic assumptions. For example, the unit emission rate of 1 g/sec from the entire facility was assumed to be emitted continuously over the modeled 5-year period. Assuming a continuous emission rate is standard modeling procedure in instances where there is no basis for allocating variable emissions. Further, knowing the specific variability of emissions is much less important when calculating a long-term average. Since site-specific process emissions were not available and a unit emission rate was used, the facility's ambient impact on annual average air-Mn concentrations may be over or under-predicted. However, the use of measured data for model calibration minimized this limitation.

Conclusions

Exposure estimates can be derived directly from modeling facility emissions or can be extrapolated from other methods when emissions data are unavailable. In instances where limited outdoor monitoring data are available, modeling using generic emission rates can yield important information about the relative magnitude of exposure within a geographic area. Using measured and modeled data, outdoor exposure concentrations of ambient air-Mn were calculated for individual study participants of two Ohio communities. This method for estimating personal exposures can prove useful in future studies to assess the relationship between adverse health

outcomes and personal exposures to environmental pollutants, where the collection of such data is unfeasible and limited air monitoring data are available.

The methods outlined in this paper can be used to estimate outdoor air-Mn exposures at receptor points when personal monitoring data are limited. This approach may yield more useful ways to estimate exposure than assuming equal exposures to nearby monitoring stations or by collecting a few days of personal air sampling data. It reflects seasonal and temporal variability and can be used to produce individual chronic estimates of outdoor exposure for receptors. Further work should be conducted to examine relationships between indoor and outdoor Mn concentrations and to evaluate how macro-environment Mn exposures are related to outdoor air-Mn exposure. Micro-environment exposure allocation to overall exposures would be invaluable to understanding the most important aspects of individual exposures at home, school, and in the workplace.

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Abbreviations and definitions:

AERMAP – AERMOD Terrain Preprocessor; AERMET – AERMOD Meteorological Preprocessor; AERMOD – AMS/EPA Regulatory Model; Air-Mn – Air Manganese; AM – arithmetic mean; AQS – Air Quality System; ATSDR – Agency for Toxic Substances and Disease Registry; GM – geometric mean; Mn – Manganese; MRL – Minimal Risk Level; NWS

– National Weather Service; NCDC – National Climatic Data Center; NEIC – National Enforcement Investigations Center; Ohio EPA – Ohio Environmental Protection Agency; RfC – Reference Concentration; TSP – Total Suspended Particulate; U.S. EPA – United States Environmental Protection Agency; WCCC – Washington County Career Center

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Implications

Few available studies evaluate long-term health outcomes from inhalational manganese (Mn) exposure in residential populations, due in part to challenges in measuring individual exposures.

Local long-term air measurements provide the means to calibrate models used in estimating long-term exposures. Furthermore, this combination of modeling and ambient air sampling can be used to derive receptor-specific exposure estimates even in the absence of source emission data for use in human health outcome studies.

Table 1. TSP air-Mn[a] Summary Statistics for Marietta Monitoring Sites (Jan. 2003-Oct. 2013)[b].

Monitoring Site	BKR (monthly avg)	WCCC (monthly avg)	Harmar (monthly avg)	Boaz (monthly avg)	Neale (monthly avg)
Distance to source facility	1.6 km	7.2 km	6.4 km	1.6 km	7.2 km
Number of observations	25	131	77	12	12
Min	0.05	0.01	0.02	0.05	0.04
Max	1.30	1.50	0.38	0.27	0.33
25th Percentile	0.16	0.05	0.06	0.10	0.09

50th Percentile	0.31	0.11	0.10	0.12	0.18
75th Percentile	0.53	0.19	0.14	0.24	0.21
Arithmetic Mean	0.39	0.14	0.11	0.15	0.16
Geometric Mean	0.28	0.09	0.09	0.13	0.14
% observations > U.S. EPA RfC (0.05 μg/m^3)	96.0	74.2	80.5	91.7	83.3
% observations > ATSDR MRL (0.30 μg/m^3)	52.0	10.2	1.3	0.0	8.3

[a]Mn concentration in micrograms per cubic meter air (μg/m3).

[b]BKR = the Blue Knob Road Site (OH); WCCC = Washington County Career Center Site (OH); Harmar = Harmar Village Site (OH);

Boaz = Boaz Waste Water Treatment Facility Site (WV); Neale = Neale Elementary School Site (WV).

Table 2. TSP air-Mn[a] Summary Statistics for East Liverpool Monitoring Sites (Jan. 2003-Oct. 2013).

Monitoring Site	Water Plant (24 hr avg)[b]	Water Plant (monthly avg)	Port Authority (monthly avg)	Maryland Ave (monthly avg)
Distance to source facility	0.08 km	0.08 km	2 km	2.1 km
Number of observations	740	132	132	132
Min	0.02	0.10	0.02	0.01
Max	25.00	6.80	1.90	1.00
25th Percentile	0.19	0.61	0.11	0.06

50th Percentile	0.54	1.05	0.19	0.12
75th Percentile	1.58	1.80	0.35	0.23
Arithmetic Mean	1.50	1.42	0.27	0.17
Geometric Mean	0.56	1.01	0.19	0.12
% observations > U.S. EPA RfC (0.05 µg/m^3)	97.0	100.0	94.6	83.9
% observations > ATSDR MRL (0.30 µg/m^3)	55.2	90.0	30.0	14.6

[a]Mn concentration in micrograms per cubic meter air (µg/m3).

[b]Collected Jan. 2005-Oct. 2013

Table 3. Distributions of TSP air-Mn[a]: comparison between estimates from the *site-surface area emissions method* model and the measured outdoor TSP air-Mn data for all monitoring sites in Marietta and East Liverpool, Ohio (2003-2013).

	Marietta		East Liverpool	
	Modeled	**Measured[b]**	**Modeled**	**Measured[b]**
Min	0.03	0.01-0.05	0.014	0.01-0.10
Max	1.61	0.27-1.50	6.32	1.00-6.80
25th Percentile	0.13	0.05-0.16	0.20	0.06-0.61
50th Percentile	0.17	0.10-0.31	0.31	0.12-1.05
75th Percentile	0.20	0.14-0.53	1.05	0.23-1.80
Geometric mean	0.17	0.09-0.28	0.35	0.12-1.01

Arithmetic mean	0.21	0.11-0.39	0.88	0.17-1.42

[a]Mn concentration in micrograms per cubic meter air (μg/m3).

[b]Calculated with monthly composite data.

Table 4. Estimates[a] of Annual Average TSP, PM_{10}, and $PM_{2.5}$ air-Mn[b] in Marietta and East Liverpool (2003-2013).

	Estimated TSP Mn		**Estimated PM_{10} Mn**		**Estimated $PM_{2.5}$ Mn**	
	Marietta	**East Liverpool**	**Marietta**	**East Liverpool**	**Marietta**	**East Liverpool**
Min	0.033	0.014	0.028	0.005	0.007	0.001
Max	1.607	6.321	1.334	2.212	0.338	0.234

25th percentile	0.134	0.196	0.112	0.069	0.028	0.007
50th percentile	0.167	0.307	0.138	0.108	0.035	0.011
75th percentile	0.201	1.047	0.167	0.367	0.042	0.039
90th percentile	0.266	2.853	0.220	0.999	0.056	0.106
95th percentile	0.761	3.364	0.632	1.177	0.160	0.124
Geometric mean	0.171	0.351	0.142	0.123	0.036	0.013
Arithmetic mean	0.214	0.878	0.177	0.307	0.045	0.033

[a] According to the "site-surface area emissions method" model.

[b]Mn concentration in micrograms per cubic meter air (μg/m3).

Table 5. TSP air-Mn[a] in Marietta, OH [b]: Comparison between traditional dispersion modeling, *site-surface area method* modeling, and rolling 5-year long-term measured average.

Monitoring Location	Facility-specific emissions model	Site-surface area emissions method	Long-term[c] measured average	Ratio of measured/facility-specific emissions model concentrations	Ratio of measured/site-surface area emissions method concentrations
WCCC[d]	0.14	0.16[e]	0.16[e]	1.14	1.00
Harmar Village	0.16	0.18	0.11	0.69	0.61

[a] Mn concentration in micrograms per cubic meter air (µg/m3).

[b] The site-surface area method averages shown here were calculated using the Washington Career Center as the reference monitor at this site.

[c] The long term average includes the average of all monthly composite measurements at each site.

[d] WCCC: Washington County Career Center.

[e] Note that the-site surface area emissions method is perfectly correlated with the actual measured concentration because the WCCC monitor is the reference location in Marietta.

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